



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 725 126 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

07.08.1996 Bulletin 1996/32

(51) Int. Cl.⁶: C10G 45/02, C10G 65/16

(21) Application number: 96101595.5

(22) Date of filing: 05.02.1996

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 03.02.1995 JP 37764/95

(71) Applicant: MITSUBISHI OIL CO., LTD.
Minato-ku Tokyo (JP)

(72) Inventors:

- Hatanaka, Shigeto,
Sunny Hill Imajuku 26-102
Yokohama-shi, Kanagawa (JP)

- Takizawa, Masaki
Aoba-ku, Sendai-shi, Miyagi 981 (JP)
- Sadakane, Osamu
Tokyo (JP)

(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem.
et al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
81925 München (DE)

(54) Process for desulfurizing catalytically cracked gasoline

(57) An efficient process for desulfurizing catalytically cracked gasoline, in which a reduction in olefin content is controlled to thereby minimize a reduction in octane number. A catalytically cracked gasoline is separated into a plurality of fractions including one or both of a fraction rich in sulfur compounds that are hard to desulfurize and a fraction rich in sulfur compounds that are easy to desulfurize. One or both of the fractions are subjected to hydrodesulfurization. The resulting fractions are then mixed with the remaining fractions.

EP 0 725 126 A1

Description

FIELD OF THE INVENTION

5 The present invention relates to a process for desulfurizing catalytically cracked gasoline. More particularly, the present invention relates to a process for hydrodesulfurizing catalytically cracked gasoline containing sulfur compounds and olefin components in the presence of a catalyst.

BACKGROUND OF THE INVENTION

10 In the field of petroleum refining, catalytically cracked gasoline is a stock of high-octane number gasoline containing a certain amount of olefin components. Catalytically cracked gasoline is a gasoline fraction obtained by catalytically cracking a heavy petroleum fraction as a stock oil, such as a vacuum gas oil or an atmospheric residual oil, and recovering and distilling the catalytically cracked products. Catalytically cracked gasoline is a primary blending stock of automotive gasoline.

15 However, the stock oil for catalytic cracking has a relatively high content of sulfur compounds. When an untreated stock oil is subjected to catalytic cracking, the resulting catalytically cracked gasoline also has a high sulfur compound content. The resulting gasoline fraction would cause environmental pollution if used as a blending stock of automotive gasoline.

20 Consequently, the stock oil is usually subjected to a desulfurization process prior to catalytic cracking.

On the other hand, a naphtha fraction obtained by distilling crude oil is generally subjected to catalytic reforming to at least partially aromatize the same and increase its octane number. Because a reforming catalyst is generally poisoned by sulfur compounds, the naphtha fraction should also be desulfurized prior to catalytic reforming.

25 A hydrodesulfurization process has hitherto been carried out to achieve the above-noted desulfurization in the field of petroleum refining. A hydrodesulfurization process includes contacting a stock oil to be desulfurized with an appropriate catalyst for hydrodesulfurization in a pressurized hydrogen atmosphere at a high temperature.

30 Catalysts which are typically used for hydrodesulfurization of heavy petroleum fractions, such as a stock oil for catalytic cracking (e.g., a vacuum gas oil or an atmospheric residual oil) and a stock oil for thermal cracking (e.g., a vacuum residual oil), comprise a group VIII element (e.g., cobalt and nickel) and a group VI element (e.g., chromium, molybdenum and tungsten) supported on an appropriate carrier (e.g., alumina). The hydrodesulfurization process is usually conducted at a temperature of about 300 to about 400°C, a hydrogen partial pressure of about 30 to about 200 kg/cm², and a liquid hourly space velocity (hereinafter abbreviated as LHSV) of about 0.1 to about 10 l/hr.

35 Catalysts which are typically used for hydrodesulfurization of naphtha comprise a combination of a group VIII element and a group VI element (e.g., a combination of cobalt and molybdenum) supported on an appropriate carrier (e.g., alumina). The hydrodesulfurization process is usually carried out at a temperature of about 280 to about 350°C, a hydrogen partial pressure of about 15 to about 40 kg/cm², and an LHSV of about 2 to about 8 l/hr.

40 In the case of hydrodesulfurization of a heavy petroleum fraction such as a vacuum gas oil or an atmospheric residual oil, which is a stock oil for catalytic cracking, processing is carried out at high temperature and high pressure as described above. Consequently, strict conditions are imposed on the apparatus design. Furthermore, an extension of the apparatus to increase its capacity involves high construction costs.

45 On the other hand, when catalytically cracked gasoline is hydrodesulfurized under the above-described processing conditions, the olefin components present in the cracked gasoline fraction are hydrogenated to reduce the olefin content, and the resulting cracked gasoline fraction has a reduced octane number. Therefore, the cracked gasoline fraction following hydrodesulfurization is desirably subjected to catalytic reforming, isomerization, etc. so as to increase the octane number. That is, two processes are involved. The technique disclosed in the unexamined published Japanese patent application No. Hei. 6-509830 based on a PCT application is an example of such a two process system.

SUMMARY OF THE INVENTION

50 An object of the present invention is to provide a process for effectively hydrodesulfurizing catalytically cracked gasoline containing sulfur compounds and olefin components while minimizing the reduction of olefin components.

In order to solve the above-described problem, the present inventors sought to develop a hydrodesulfurization process for removing sulfur compounds to a permissible level while minimizing reduction in the content of olefin components. As a result, the present inventors found that various sulfur compounds contained in catalytically cracked gasoline are not equally hydrodesulfurized, and the ease or difficulty in desulfurization varies depending on the molecular structure of the sulfur compounds.

In view of the difference in the relative ease or difficulty in desulfurization among sulfur compounds, the present inventors have discovered a process for hydrodesulfurizing catalytically cracked gasoline containing sulfur compounds and olefin components, which comprises separating the catalytically cracked gasoline into a plurality of fractions includ-

5 ing at least one of (i) a first fraction rich in sulfur compounds that are hard to desulfurize and (ii) a second fraction rich in sulfur compounds that are easy to desulfurize, next hydrodesulfurizing at least one of the first and second fractions in the presence of a catalyst, and then mixing the hydrodesulfurized fraction(s) with the remaining fractions. That is, the present invention relates to a process for desulfurizing catalytically cracked gasoline comprising separating the catalytically cracked gasoline into at least one of a fraction that has a high content of a single or a plurality of sulfur compounds that are difficult to desulfurize and a fraction that has a high content of a single or a plurality of sulfur compounds that are easy to desulfurize, subjecting at least one of the fractions to hydrodesulfurization under optimum conditions, and mixing the fractions.

10 DETAILED DESCRIPTION OF THE INVENTION

The catalytically cracked gasoline for use in the present invention is a gasoline fraction distilled at a temperature of from about 30 to about 250°C. The catalytically cracked gasoline is obtained by catalytically cracking a heavy petroleum fraction (e.g., a vacuum gas oil or an atmospheric residual oil) to mostly convert the heavy petroleum fraction into a broad range of petroleum fractions, and recovering and distilling the catalytically cracked products. The catalytically cracked gasoline is often separated into a light fraction and a heavy fraction which are used depending on the intended application as a gasoline base. The boiling point of the light fraction is from about 30 to about 180°C, and that of the heavy fraction is from about 80 to about 250°C.

20 These catalytically cracked gasoline fractions contain about 10 to about 1000 ppm of sulfur compounds, such as thiophene, alkylthiophenes, benzothiophene, alkylbenzothiophenes, thiacyclopentane, alkylthiacyclopentanes, mercaptanes and sulfides. Catalytically cracked gasoline which has been subjected to sweetening also contains disulfides. These sulfur compounds can be analyzed and quantified by a GC-AED (a gas chromatography with an atomic emission detector).

25 Of these sulfur compounds, thiophene and alkylthiophenes are compounds that are difficult to desulfurize. Alkylthiophenes are more difficult to desulfurize than thiophene. The alkylthiophenes become more difficult to desulfurize with an increase in the number of constituent alkyl groups. The present invention is characterized in that one or more sulfur compounds which are difficult to desulfurize are identified as such, and one or more fractions having a high concentration of sulfur compounds that are hard to desulfurize are handled separately from other fractions.

30 On the other hand, benzothiophene, alkylbenzothiophenes, thiacyclopentane, and alkylthiacyclopentanes, among the above-described sulfur compounds, are examples of sulfur compounds that are easy to desulfurize. Of these, benzothiophene is the easiest to desulfurize. The alkylbenzothiophenes become more difficult to desulfurize with an increase in the number of constituent alkyl groups.

35 Separating the catalytically cracked gasoline into a fraction that is rich in sulfur compounds that are hard to desulfurize and into a fraction that is rich in sulfur compounds that are easy to desulfurize may be accomplished by any of distillation, adsorption, crystallization and the like. Distilling is the most convenient of these methods.

The boiling points of typical sulfur compounds that are hard to desulfurize are as follows. Thiophene: 84.16°C; 2-methylthiophene: 112.56°C; 3-methylthiophene: 115.44°C; 2-ethylthiophene: 134.00°C; 3-ethylthiophene: 136.00°C; 2,5-dimethylthiophene: 136.70°C; 2,4-dimethylthiophene: 140.70°C; 2,3-dimethylthiophene: 141.60°C; 3,4-dimethylthiophene: 145.00°C; 2-isopropylthiophene: 153.00°C; 3-isopropylthiophene: 157.00°C; 3-ethyl-2-methylthiophene: 157.00°C; 5-ethyl-2-methylthiophene: 160.10°C; 2,3,5-trimethylthiophene: 164.50°C; and 2,3,4-trimethylthiophene: 172.70°C.

40 The boiling points of typical sulfur compounds that are easy to desulfurize are as follows. Thiacyclopentane: 121.12°C; 2-methylthiacyclopentane: 133.23°C; 3-methylthiacyclopentane: 138.64°C; 2,trans-5-dimethylthiacyclopentane: 142.00°C; 2,cis-5-dimethylthiacyclopentane: 142.28°C; 3,3-dimethylthiacyclopentane: 145.00°C; 2,3-dimethylthiacyclopentane: 148.00°C; 3-ethylthiacyclopentane: 165.00°C; benzothiophene: 219.90°C; methylbenzothiophene: 243.90°C.

45 Thus, some of the sulfur compounds that are hard to desulfurize and some of the sulfur compounds that are easy to desulfurize have boiling points that are close together. Accordingly, it is necessary to first determine the distribution of sulfur compounds by analysis, and to then select a distillation apparatus and distillation conditions that would provide the greatest degree of separation possible. After separation, the fraction that is rich in sulfur compounds that are hard to desulfurize desirably contains sulfur compounds that are hard to desulfurize in an amount of more than 50 mol%, preferably at least 60 mol%, of the total sulfur compound content. Likewise, the fraction that is rich in sulfur compounds that are easy to desulfurize desirably contains sulfur compounds that are easy to desulfurize in an amount of more than 50 mol%, preferably at least 60 mol%, of the total sulfur compound content. To separate a sample containing both sulfur compounds that are hard to desulfurize and sulfur compounds that are easy to desulfurize having close boiling points, a multi-stage distillation apparatus is preferred to a single distillation apparatus for carrying out separation and concentration at increased efficiency.

55 The method used for desulfurizing a fraction that is rich in sulfur compounds that are hard to desulfurize and a fraction that is rich in sulfur compounds that are easy to desulfurize is selected according to the intended purpose.

The language "rich in sulfur compounds that are hard to desulfurize" might be defined as a fraction containing sulfur compounds that are hard to desulfurize in an amount of more than 50 mol%, preferably at least 60 mol%, of the total content of sulfur compounds contained in the fraction.

The language "rich in sulfur compounds that are easy to desulfurize" might be defined as a fraction containing sulfur compounds that are easy to desulfurize in an amount of more than 50 mol%, preferably at least 60 mol%, of the total content of sulfur compounds contained in the fraction.

For example, where the sulfur content is to be reduced to a limited extent, only a fraction that is rich in sulfur compounds that are easy to desulfurize is subjected to hydrodesulfurization under mild conditions, for example, in the presence of a catalyst for hydrodesulfurization at a temperature of about 200 to about 300°C, a hydrogen partial pressure of about 5 to about 20 kg/cm², and an LHSV of about 4 to about 20 1/hr.

Hydrodesulfurization of the fraction that is rich in sulfur compounds that are easy to desulfurize can be performed while retaining the olefin components that are originally present in the fraction. More particularly, if proper reaction conditions are selected, a desulfurization rate as high as 70% or even more can be achieved while controlling hydrogenation of the olefins to 10% by volume or lower, thus minimizing a reduction in octane number.

It is necessary to select the conditions of hydrodesulfurization for each fraction, taking into consideration the kinds and amounts of sulfur compounds contained therein and the kinds and amounts of olefin components concurrently contained therein, in order to achieve the desired desulfurization rate and a permissible reduction in octane number.

The reaction conditions of hydrodesulfurization are selected from a temperature range of from about 200 to about 350°C, a hydrogen partial pressure range of from about 5 to about 30 kg/cm², an LHSV range of from about 1 to about 20 1/hr, and a hydrogen/oil ratio range of from about 300 to about 5000 scf/bbl. The lower the temperature or pressure, or the higher the hydrogen/oil ratio, the more effectively olefin hydrogenation can be suppressed to minimize a reduction in octane number.

On the other hand, where a high overall rate of desulfurization is required, both a fraction that is rich in sulfur compounds that are hard to desulfurize and a fraction that is rich in sulfur compounds that are easy to desulfurize are subjected to hydrodesulfurization. In this case, the conditions of hydrodesulfurization are optimized for each fraction to achieve the desired high rate of desulfurization while controlling hydrogenation of olefins to minimize a reduction in octane number.

The catalyst for use in the present invention includes those ordinarily used for hydrodesulfurization in the field of petroleum refining. That is, the catalyst generally comprises a desulfurization active metal supported on a porous inorganic oxide carrier.

The porous inorganic oxide carrier includes alumina, silica, titania, magnesia and mixtures thereof. Alumina and silica-alumina are preferred.

The desulfurization active metal includes chromium, molybdenum, tungsten, cobalt, nickel and mixtures thereof. Cobalt-molybdenum and nickel-cobalt-molybdenum are preferred. These metals can have the form of a metal, an oxide, a sulfide or a mixed form thereof on the carrier. The active metal can be supported on the carrier by a known method, such as impregnation or co-precipitation.

In the present invention, a catalyst comprising cobalt-molybdenum or nickel-cobalt-molybdenum supported on an alumina carrier is preferred. The amount of the active metal supported on the oxide carrier is preferably about 1 to about 30% by weight, more preferably about 3 to about 20% by weight, in terms of the oxide of the active metal. The metals may be preliminarily converted to sulfides in a known manner before use in hydrogenation.

The reaction tower for hydrogenation may be of a fixed bed type, a fluidized bed type or a boiling bed type. A fixed bed type reactor is preferred. The catalytically cracked gasoline fraction can be contacted with the catalyst in any of a parallel upward flow system, a parallel downward flow system or a countercurrent flow system. These operations are well known in the field of petroleum refining, and known techniques can be selected as appropriate.

EXAMPLES

The present invention will now be illustrated in greater detail by way of the following Examples. However, the present invention should not be construed as being limited to those Examples.

COMPARATIVE EXAMPLE 1

A catalytically cracked gasoline light fraction (about a 30 to 80°C fraction) was obtained by catalytically cracking a stock oil containing an atmospheric residual oil. The term "about a 30 to 80°C fraction" as used herein is a nominal designation. This fraction actually contained 11.9% by weight of a fraction having a boiling point of 30°C or lower and 3.2% by weight of a fraction having a boiling point exceeding 80°C (hereinafter referred to as an 80+°C cut) as shown in Table 1 below. The about a 30 to 80°C fraction had a density of 0.675 g/cm³ at 15°C, a sulfur content of 27 ppm, an olefin content of 65% by volume, and a research method octane number of 93.8.

5 A commercially available catalyst comprising an alumina carrier having supported thereon 5% by weight of CoO and 17% by weight of MoO₃ was used for hydrodesulfurization after it was preliminarily converted to a sulfide form in a usual manner. The above-described catalytically cracked gasoline fraction was hydrodesulfurized using a fixed bed parallel downward flow type hydrogenation reaction apparatus under relatively mild conditions, i.e., at a reaction temperature of 250°C, a partial hydrogen pressure of 10 kg/cm², an LHSV of 5 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

10 As a result, a hydrodesulfurized catalytically cracked gasoline light fraction was obtained having a sulfur content of 12 ppm, an olefin content of 44% by volume, and a research method octane number of 86.1. There was no loss of liquid components due to the treatment.

15 **EXAMPLE 1**

The same catalytically cracked gasoline as used in Comparative Example 1 was distilled to divide the same into 7 cuts each by a difference in distillation temperature of 10°C. The yield, sulfur content and olefin content of each cut are shown in Table 1 below.

20

Distillation Temperature (°C)	Yield (wt%)	Sulfur Content (ppm)	Olefin Content (vol%)
I.B.P. to 30	11.9	0	82
30 to 40	36.0	1	73
40 to 50	1.9	7	84
50 to 60	7.7	3	42
60 to 70	28.3	24	55
70 to 80	11.0	129	62
80+	3.2	154	51
total	100.0	27	65

30

35 On analysis of the sulfur content of the 70 to 80°C cut, it was found that 90 mol% of the sulfur content was thiophene, a sulfur compound that is hard to desulfurize. Analysis of the sulfur content of the 80+°C cut revealed that 94 mol% of the sulfur content also was thiophene. The 70 to 80°C cut and 80+°C cut which were rich in sulfur compounds that are hard to desulfurize were mixed together and hydrodesulfurized using the same reaction apparatus and the same catalyst as used in Comparative Example 1 at a temperature of 300°C, a hydrogen partial pressure of 30 kg/cm², an LHSV of 5 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

40 The mixture of the 70 to 80°C cut and the 80+°C cut had a sulfur content of 145 ppm and an olefin content of 59% by volume. The hydrodesulfurization treatment reduced the sulfur content and the olefin content to 3 ppm and 5% by volume, respectively. The treated oil was added to the remaining cuts to obtain catalytically cracked gasoline having a sulfur content of 8 ppm, an olefin content of 62% by volume, and a research method octane number of 91.8. There was no loss of liquid components due to the treatment.

45 **EXAMPLE 2**

50 The same catalytically cracked gasoline as used in Comparative Example 1 was distilled into 7 cuts each by a difference in distillation temperature of 10°C in the same manner as in Example 1. The 70 to 80°C cut and the 80+°C cut rich in sulfur compounds that are hard to desulfurize were mixed and treated under the same conditions as in Example 1.

55 Separately, as a result of analysis, 95 mol% of the sulfur content of the 60 to 70°C cut was found to be n-propylmercaptane. The 60 to 70°C cut was hydrodesulfurized using the same apparatus and catalyst as used in Comparative Example 1 at a reaction temperature of 250°C, a hydrogen partial pressure of 5 kg/cm², an LHSV of 5 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

The sulfur content and the olefin content of the 60 to 70°C cut were 24 ppm and 55% by volume, respectively, while those of the hydrodesulfurized oil were 5 ppm and 41% by volume, respectively.

The treated oil of the mixture of the 70 to 80°C cut and the 80+°C cut and the treated oil of the 60 to 70°C cut were added to the remaining cuts to obtain catalytically cracked gasoline having a sulfur content of 3 ppm, an olefin content

of 57% by volume, and a research method octane number of 89.5. There was no loss of liquid components due to the treatment.

COMPARATIVE EXAMPLE 2

5 A catalytically cracked gasoline whole fraction (about a 30 to 210°C fraction) obtained by catalytically cracking stock oil containing an atmospheric residual oil was used as a catalytically cracked gasoline. The term "about a 30 to 10 210°C fraction" as used herein is a nominal designation. This fraction actually contained 4.9% by weight of a fraction having a boiling point of 30°C or lower and 1.5% by weight of a fraction having a boiling point exceeding 210°C (hereinafter referred to as 210+°C cut) as shown in Table 2 below. The whole fraction had a density of 0.731 g/cm³ at 15°C, a sulfur content of 92 ppm, an olefin content of 43% by volume, and a research method octane number of 92.0.

15 A commercially available catalyst comprising an alumina carrier having supported thereon 3.8% by weight of CoO and 12.5% by weight of MoO₃ was used for hydrodesulfurization after it was preliminarily converted to a sulfide form in a usual manner. The above-described catalytically cracked gasoline was hydrodesulfurized using the same reaction apparatus as used in Comparative Example 1 under mild conditions, i.e., at a reaction temperature of 240°C, a hydrogen partial pressure of 10 kg/cm², an LHSV of 7 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

20 As a result, a hydrodesulfurized catalytically cracked gasoline whole fraction was obtained having a sulfur content of 63 ppm, an olefin content of 38% by volume, and a research method octane number of 90.3. There was no loss of liquid components due to the treatment.

COMPARATIVE EXAMPLE 3

25 The same catalytically cracked gasoline whole fraction as used in Comparative Example 2 was hydrodesulfurized under more severe conditions than those employed in Comparative Example 2, i.e., at a reaction temperature of 270°C, a hydrogen partial pressure of 10 kg/cm², an LHSV of 5 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl. The apparatus and catalyst used were the same as those used in Comparative Example 2.

30 As a result, a hydrodesulfurized catalytically cracked gasoline whole fraction was obtained having a sulfur content of 27 ppm, an olefin content of 31% by volume and a research method octane number of 87.8. There was no loss of liquid components due to the treatment.

EXAMPLE 3

35 The same catalytically cracked gasoline as used in Comparative Example 2 was distilled to obtain 20 divided cuts each different in distillation temperature by 10°C. The yield, sulfur content and olefin content of each cut are shown in Table 2.

40 As a result of analysis, it was found that: 85 mol% of the sulfur content of the 120 to 130°C cut was thiacyclopentane, a sulfur compound that is easy to desulfurize; 70 mol% of the sulfur content of the 130 to 140°C cut was C1, C2 thiacyclopentane, sulfur compounds that are easy to desulfurize; and the proportion of benzothiophene, a sulfur compound that is easy to desulfurize, of the sulfur content of the 190 to 200°C cut, 200 to 210°C cut and 210+°C cut was 85 mol%, 95 mol%, and 73 mol%, respectively.

45

50

55

TABLE 2

Distillation Temperature (°C)	Yield (wt%)	Sulfur Content (ppm)	Olefin Content (vol%)
I.B.P. to 30	4.9	0	82
30 to 40	14.8	1	73
40 to 50	0.8	7	84
50 to 60	3.2	3	42
60 to 70	11.6	24	55
70 to 80	4.5	130	60
80 to 90	2.3	151	51
90 to 100	9.5	14	50
100 to 110	4.2	93	40
110 to 120	5.5	210	32
120 to 130	4.6	60	50
130 to 140	4.2	145	27
140 to 150	7.3	160	23
150 to 160	2.0	123	35
160 to 170	6.1	153	18
170 to 180	3.6	126	17
180 to 190	3.8	185	15
190 to 200	3.0	152	16
200 to 210	2.6	340	13
210+	1.5	324	12
total	100.0	27	65

The cuts that were rich in sulfur compounds that are easy to desulfurize, i.e., the 120 to 130°C cut, 130 to 140°C cut, 190 to 200°C cut, 200 to 210°C cut, and 210+°C cut were mixed together and subjected to hydrodesulfurization 40 using the same apparatus and catalyst as used in Comparative Example 2 at a reaction temperature of 240°C, a hydrogen partial pressure of 10 kg/cm², an LHSV of 7 1/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

The mixture of the cuts rich in sulfur compounds that are easy to desulfurize had a sulfur content of 171 ppm and an olefin content of 28% by volume, which were reduced by hydrodesulfurization to 33 ppm and 26% by volume, respectively. The oil thus treated was added to the remaining cuts to obtain catalytically cracked gasoline having a sulfur 45 content of 69 ppm, an olefin content of 42.5% by volume, and a research method octane number of 91.7. There was no loss of liquid components due to the treatment.

EXAMPLE 4

50 The same catalytically cracked gasoline as used in Comparative Example 2 was distilled to obtain 20 divided cuts each different in distillation temperature by 10°C in the same manner as in Example 3. A mixture of the cuts rich in sulfur compounds that are easy to desulfurize, i.e., the 120 to 130°C cut, 130 to 140°C cut, 190 to 200°C cut, 200 to 210°C cut, and 210+°C cut, was treated under the same conditions as in Example 3.

55 As a result of analysis, it was found that: the proportion of thiophene, a sulfur compound that is hard to desulfurize, of the sulfur content of the 70 to 80°C cut and the 80 to 90°C cut was 85 mol% and 90 mol%, respectively; the proportion of methylthiophene, a sulfur compound that is hard to desulfurize, of the 110 to 120°C cut was 87 mol%; the proportion of dimethylthiophene, a sulfur compound that is hard to desulfurize, of the 140 to 150°C cut was 87 mol%; the total proportion of trimethylthiophene, methylethylthiophene, and propylthiophene, which are sulfur compounds that are hard to desulfurize, of the sulfur content of the 160 to 170°C cut was 69 mol%; and the total proportion of tetramethyl-

thiophene, dimethylethythiophene, diethylthiophene, and methylpropylthiophene, which are sulfur compounds that are hard to desulfurize, of the sulfur content of the 180 to 190°C cut was 56 mol%.

5 Those cuts rich in sulfur compounds that are hard to desulfurize, i.e., the 70 to 80°C cut, 80 to 90°C cut, 110 to 120°C cut, 140 to 150°C cut, 160 to 170°C cut, and 180 to 190°C cut were mixed and hydrodesulfurized using the same apparatus and catalyst as used in Comparative Example 2 at a reaction temperature of 300°C, a hydrogen partial pressure of 30 kg/cm², an LHSV of 5 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

10 The mixture of the cuts rich in sulfur compounds that are hard to desulfurize had a sulfur content of 166 ppm and an olefin content of 31% by volume, which were reduced to 14 ppm and 4% by volume, respectively, by the hydrodesulfurization treatment. The treated oil was added to the remaining cuts to obtain catalytically cracked gasoline having a sulfur content of 25 ppm, an olefin content of 35% by volume, and a research method octane number of 89.2. There was no loss of liquid components by the treatment.

COMPARATIVE EXAMPLE 4

15 A catalytically cracked gasoline whole fraction (about a 30 to 230°C fraction) was obtained by catalytically cracking a stock oil containing an atmospheric residual oil. The whole fraction had a density of 0.748 g/cm³ at 15°C, a sulfur content of 352 ppm, an olefin content of 38% by volume, and a research method octane number of 91.7. The whole fraction was hydrodesulfurized using the same apparatus and catalyst as in Comparative Example 1 at a reaction temperature of 250°C, a hydrogen partial pressure of 10 kg/cm², an LHSV of 7 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

20 As a result, a hydrodesulfurized catalytically cracked gasoline whole fraction was obtained having a sulfur content of 115 ppm, an olefin content of 33% by volume, and a research method octane number of 89.4. There was no loss of liquid components due to the treatment.

EXAMPLE 5

25 The same catalytically cracked gasoline as used in Comparative Example 4 was divided by distillation into a 30 to 100°C cut and a 100 to 230°C cut. The ratio of the 30 to 100°C cut to the whole fraction was 32% by weight, and the 30 to 100°C cut had a sulfur content of 62 ppm and an olefin content of 53% by volume. The ratio of the 100 to 230°C cut to the whole fraction was 68% by weight, and the 100 to 230°C cut had a sulfur content of 488 ppm and an olefin content of 31% by volume. The sulfur content of the 100 to 230°C cut was found by analysis to consist of 28 mol% of benzothiophene, 31 mol% of methylbenzothiophene, 2 mol% of thiacyclopentane, and 3 mol% of methylthiacyclopentane, which are sulfur compounds that are easy to desulfurize, and the balance of thiophene compounds which are sulfur compounds that are hard to desulfurize.

30 The 100 to 230°C cut rich in sulfur compounds that are easy to desulfurize was hydrodesulfurized using the same apparatus and catalyst as used in Comparative Example 1 at a reaction temperature of 250°C, a hydrogen partial pressure of 10 kg/cm², an LHSV of 5 l/hr, and a hydrogen/oil ratio of 1000 scf/bbl.

35 By carrying out the hydrodesulfurization treatment, the sulfur content and the olefin content were reduced to 135 ppm and 28% by volume, respectively. The treated oil was mixed with the 30 to 100°C cut to obtain catalytically cracked gasoline having a sulfur content of 112 ppm, an olefin content of 36% by volume, and a research method octane number of 90.5. There was no loss of liquid components due to the treatment.

40 The catalytic hydrodesulfurization process for treating catalytically cracked gasoline containing sulfur compounds and olefin components according to the present invention is characterized in that the catalytically cracked gasoline is separated into a fraction rich in sulfur compounds that are hard to desulfurize and a fraction rich in sulfur compounds that are easy to desulfurize. One or both of the fractions are subjected to hydrodesulfurization under optimum conditions, and the fractions are then mixed together again. The process of the present invention makes it possible to efficiently desulfurize stock oil while suppressing a reduction in olefin content, to thereby minimize a reduction in octane number.

45 It should further be apparent to those skilled in the art that various changes in form and detail of the invention as shown and described above may be made. It is intended that such changes be included within the spirit and scope of the claims appended hereto.

Claims

50 1. A process for hydrodesulfurizing catalytically cracked gasoline containing sulfur compounds and olefin components, which comprises separating the catalytically cracked gasoline into a plurality of fractions including at least one of (i) a first fraction rich in sulfur compounds that are hard to desulfurize and (ii) a second fraction rich in sulfur compounds that are easy to desulfurize, next hydrodesulfurizing at least one of the first and second fractions in the presence of a catalyst, and then mixing the fractions.

2. The process of claim 1, wherein said separating step comprising separating the catalytically cracked gasoline into a plurality of fractions including (i) at least one fraction rich in sulfur compounds that are hard to desulfurize and (ii) at least one fraction rich in sulfur compounds that are easy to desulfurize.
- 5 3. The process of claim 1 or 2, wherein said separating step comprises distilling.
4. The process of any one of claims 1 to 3, wherein the only fraction that is subjected to hydrodesulfurization is said second fraction.
- 10 5. The process of any one of claims 1 to 4, wherein said hydrodesulfurizing step comprises hydrodesulfurizing said second fraction while controlling the degree of hydrogenation of the olefin components contained in said fraction to 10% by volume or lower.
- 15 6. The process of any one of claims 1 to 3, wherein the only fraction that is subjected to hydrodesulfurization is said first fraction.
7. The process of any one of claims 1 to 6, wherein said first fraction contains sulfur compounds that are hard to desulfurize in an amount of at least 60 mol% of the total content of sulfur compounds, and the second fraction contains sulfur compounds that are easy to desulfurize in an amount of at least 60 mol% of the total content of sulfur compounds.
- 20 8. The process of any one of claims 1 to 7, wherein said sulfur compounds that are hard to desulfurize comprise at least one of thiophene and alkylthiophene, and said sulfur compounds that are easy to desulfurize comprise at least one of thiacyclopentane, an alkylthiacyclopentane, benzothiophene and an alkylbenzothiophene.
- 25 9. The process of claim 8, wherein the alkyl group of said alkylthiophene, alkylthiacyclopentane and alkylbenzothiophene is selected from the group consisting of a methyl group, an ethyl group and a propyl group.
10. The process of any one of claims 1 to 3, 6 and 7, wherein said sulfur compounds that are hard to desulfurize comprise at least one of thiophene and methylthiophene.
- 30 11. The process of any one of claims 1 to 5 and 7, wherein said sulfur compounds that are easy to desulfurize comprise at least one of benzothiophene and methylbenzothiophene.

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 96 10 1595

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
X	FR-A-2 476 118 (IFP) * claims 1-9 *	1-11	C10G45/02 C10G65/16						
X	DE-B-10 30 952 (ESSO) * column 5, line 35 - line 54; claims 1-4 *	1-11							
			TECHNICAL FIELDS SEARCHED (Int.Cl.)						
			C10G						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>23 May 1996</td> <td>Michiels, P</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	23 May 1996	Michiels, P
Place of search	Date of completion of the search	Examiner							
THE HAGUE	23 May 1996	Michiels, P							
<p>CATEGORY OF CITED DOCUMENTS</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top;"> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document </td> <td style="width: 50%; vertical-align: top;"> T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons A : member of the same patent family, corresponding document </td> </tr> </table>				X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons A : member of the same patent family, corresponding document				
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document	T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons A : member of the same patent family, corresponding document								